Herbert Wertheim College of Engineering
UNIVERSITY of FLORIDA

POWERING THE NEW ENGINEER TO TRANSFORM THE FUTURE

Department of Mechanical and Aerospace Engineering

Unlocking Solar Thermochemical Potential: Receivers, Reactors, and Heat Exchangers

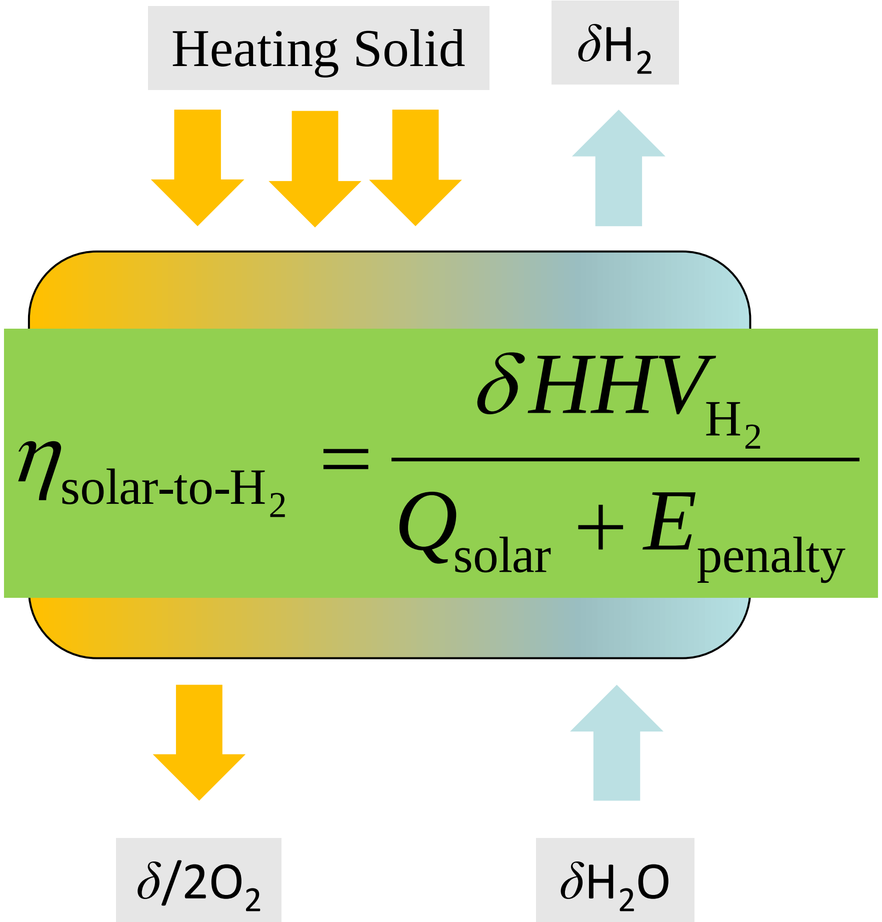
US DOE SETO - Webinar-workshop

Thursday, Dec. 3rd 2020

Jonathan Scheffe – *Renewable Energy Conversion Lab*

Questions that will be Addressed

- How do thermodynamics and kinetics contribute to solar thermochemical performance, or efficiency?
- What are the key challenges related to measuring thermodynamic and kinetic properties of thermochemical materials?
- What are overlooked chemistry-based technical metrics/objectives that should be considered at both early and late stages?



$$\eta_{\text{solar-to-H}_2} = \frac{\delta HHV_{H_2}}{Q_{\text{solar}} + E_{\text{penalty}}}$$

Large for T_{swing} cycle, $T_H > T_L$

Heating Solid Reactants $= \int_{T_L}^{T_H} c_{p,ox}\, dT$

+

Endothermic Reduction $= \Delta h_{red}\,\delta$

+

Large for **isothermal** cycle, $T_H = T_L$

Heating Fluid Reactants $= \dot{n}_{H_2O}\, \Delta h_{H_2O}\Big|_{298K \rightarrow T_L}$

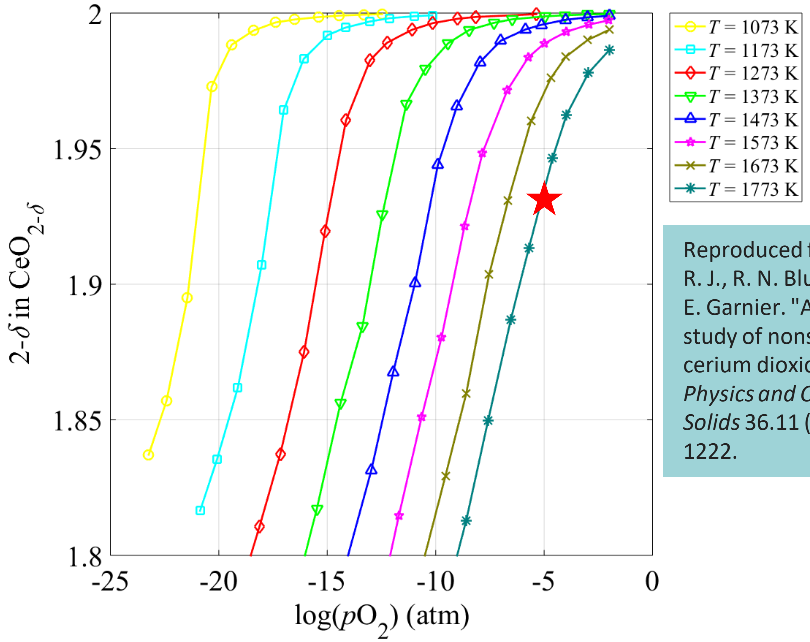
$$Q_{in} = Q_{solar}\,\eta_{abs}$$

Thermodynamic Analysis is First

- This will tell you if it is worth investigating materials to begin with
- Properties can be measured a variety if ways if data not available
- Variations in the oxidation pO_2 can result in substantial differences in fuel production and affect efficiency

$$H_2O \rightleftharpoons H_2 + 0.5O_2$$

$$\frac{pO_2}{p^\circ} = \left[K_w(T) \frac{pH_2O}{pH_2} \right]^2$$



Reproduced from: Panlener, R. J., R. N. Blumenthal, and J. E. Garnier. "A thermodynamic study of nonstoichiometric cerium dioxide." *Journal of Physics and Chemistry of Solids* 36.11 (1975): 1213-1222.

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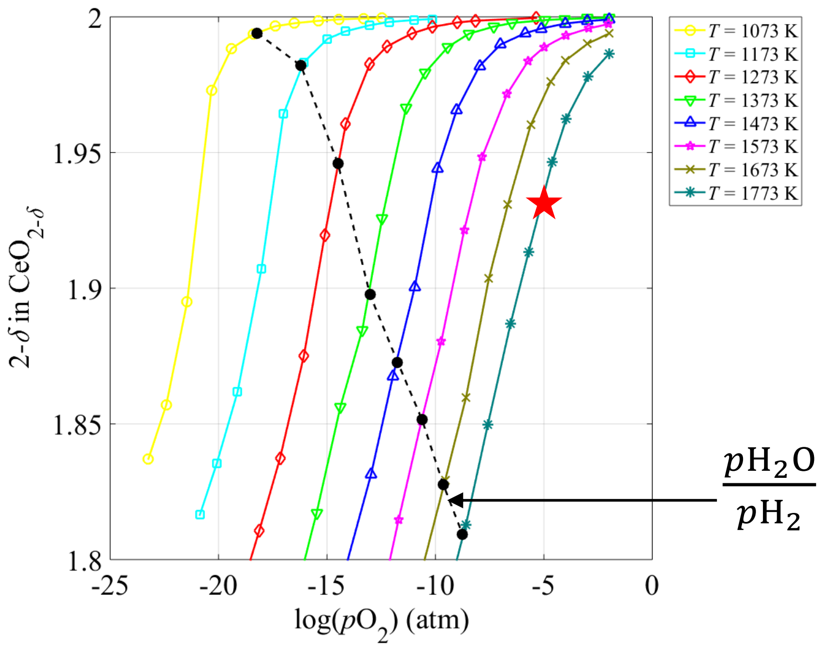

$$\frac{pH_2O}{pH_2} = 1$$

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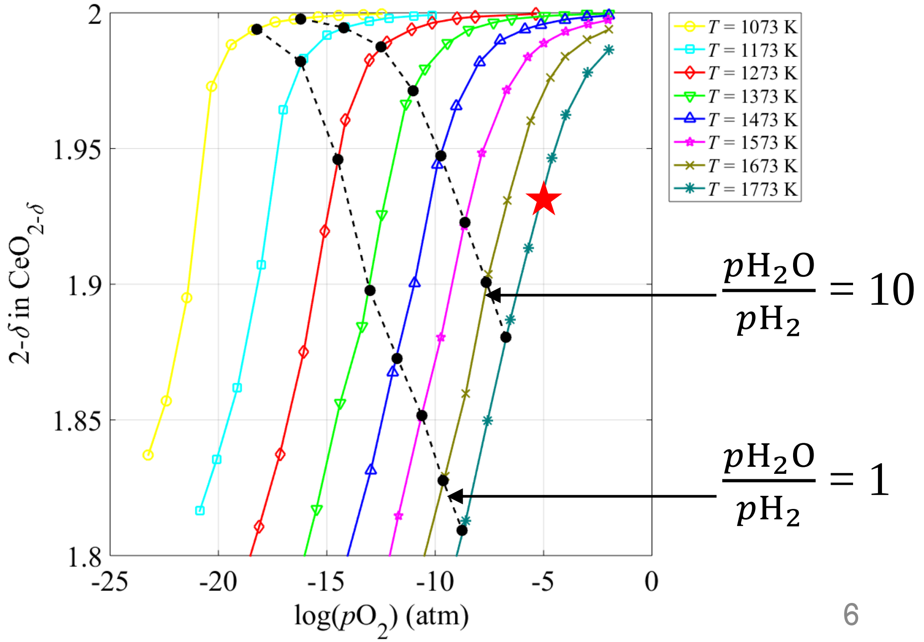

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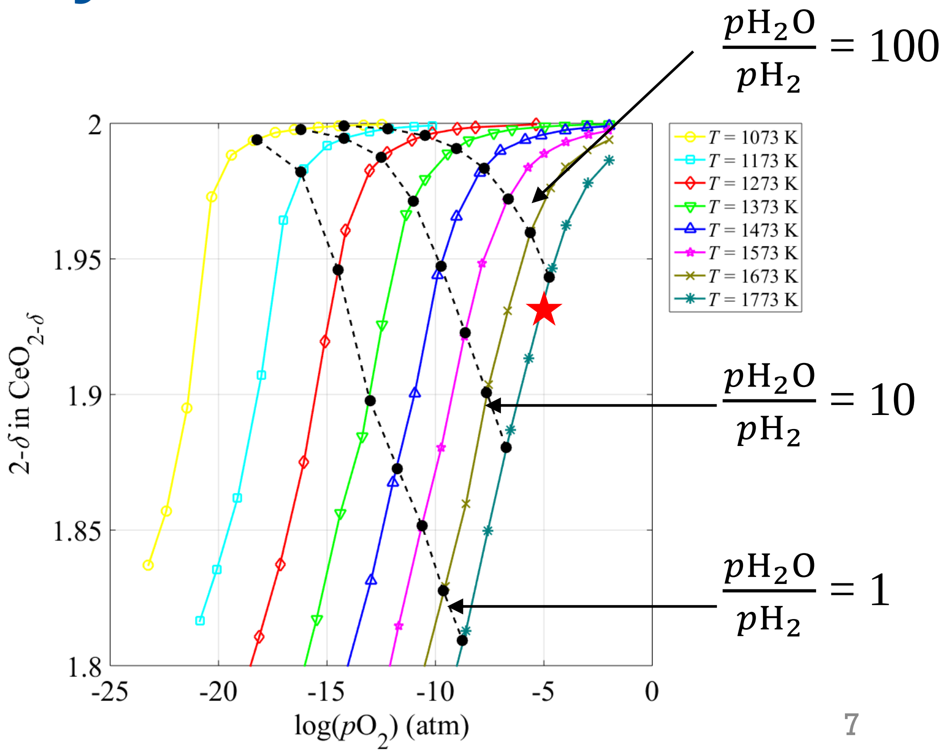
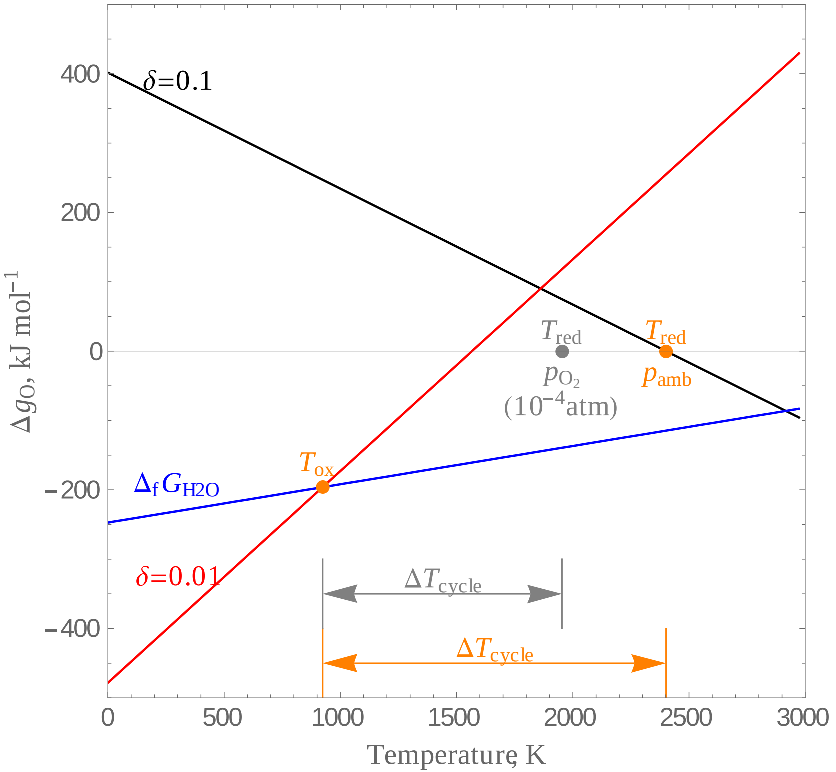


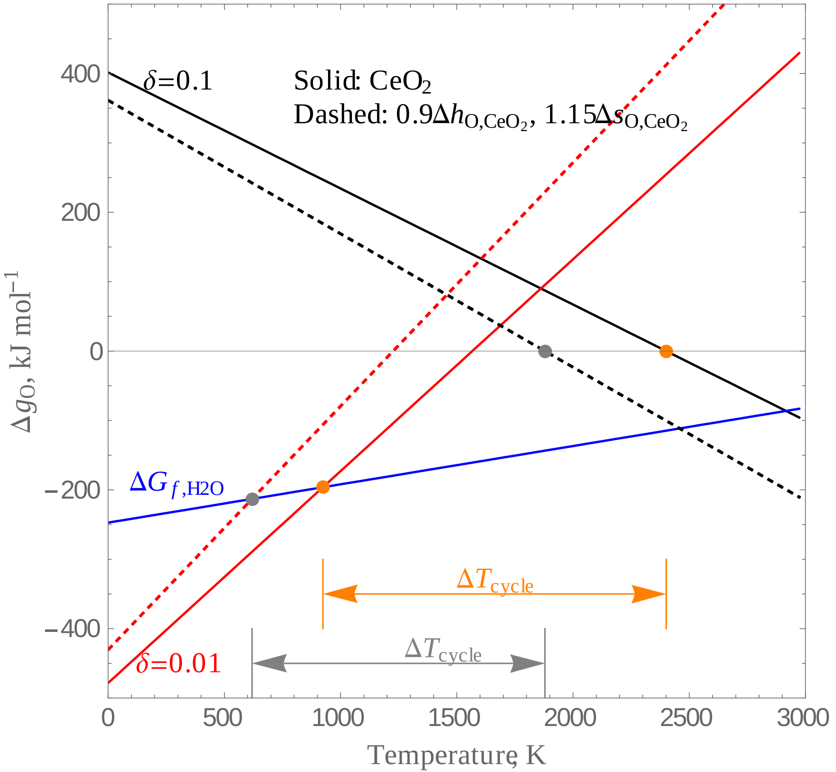
↑ Δs, ↓ Δh Most Favorable

- ΔT_{cycle} and T_{red} are driven by Δs and Δh of redox material
- Current SOA material, $CeO_{2-\delta}$, is shown to the right is used to demonstrate



↑ Δs, ↓ Δh Most Favorable

- ΔT_{cycle} and T_{red} are driven by Δs and Δh of redox material
- Current SOA material, $CeO_{2-\delta}$, is shown to the right is used to demonstrate
- Decreasing Δh and increasing Δs result in lower T_{red} and ΔT_{cycle} – see dashed lines

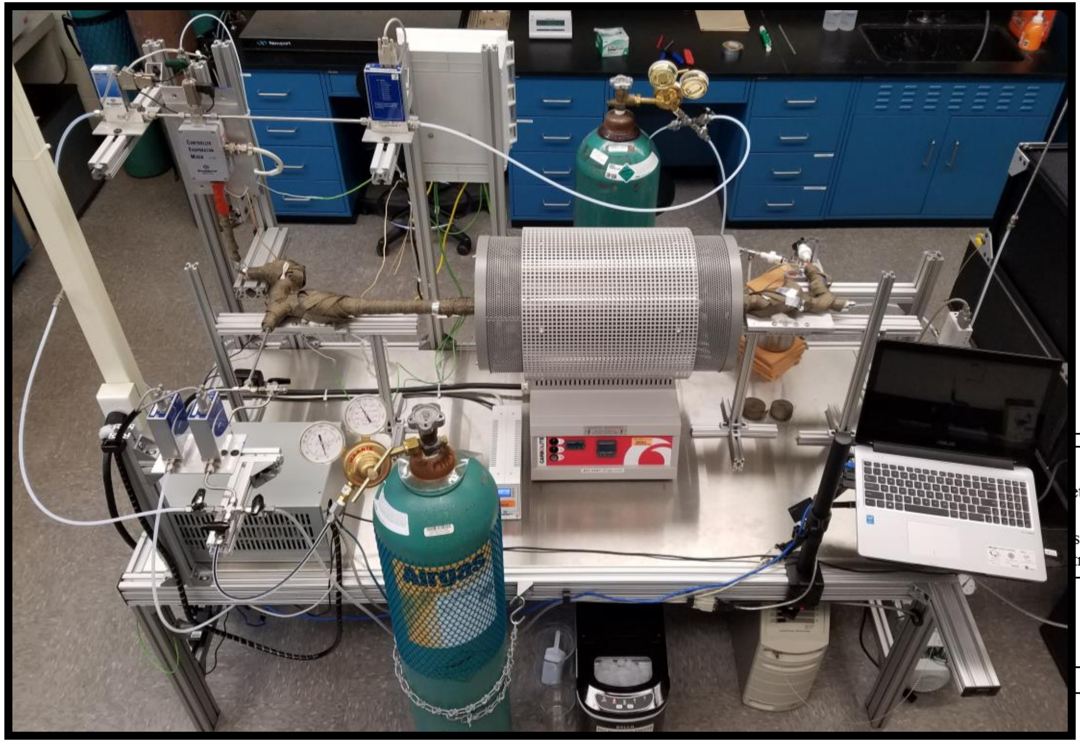


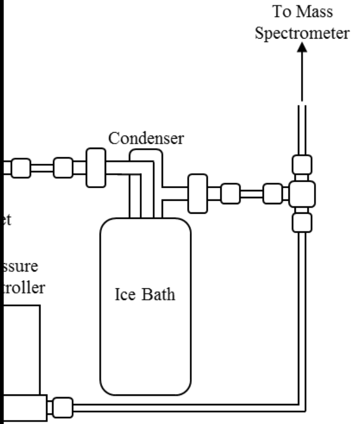
Measuring Kinetics and Thermodynamics

- It is always important to know your p_{O2} and T, but usually p_{O2} is not
  - Can be controlled by varying H_2O/H_2 in system and measuring changes in concentrations due to reduction and oxidation
  - Usually not controlled during oxidation
  - Efficiency cannot be predicted without measurements under controlled p_{O2}
- Kinetics that are modeled should be calculated from reaction rates that are free from:
  - Mass transfer limitations
  - Heat transfer limitations
  - Dispersion and detector lag
  - Large particle size distributions – as much as possible
  - Morphological changes
  - Impacted by reverse reaction (K>>1)

Controlled H_2O/H_2 HTWSR

T	293-1873 K
p_{tot}	0.2 mbar-1.01325 bar
pO_2	$f(T, pH_2, pH_2O)$



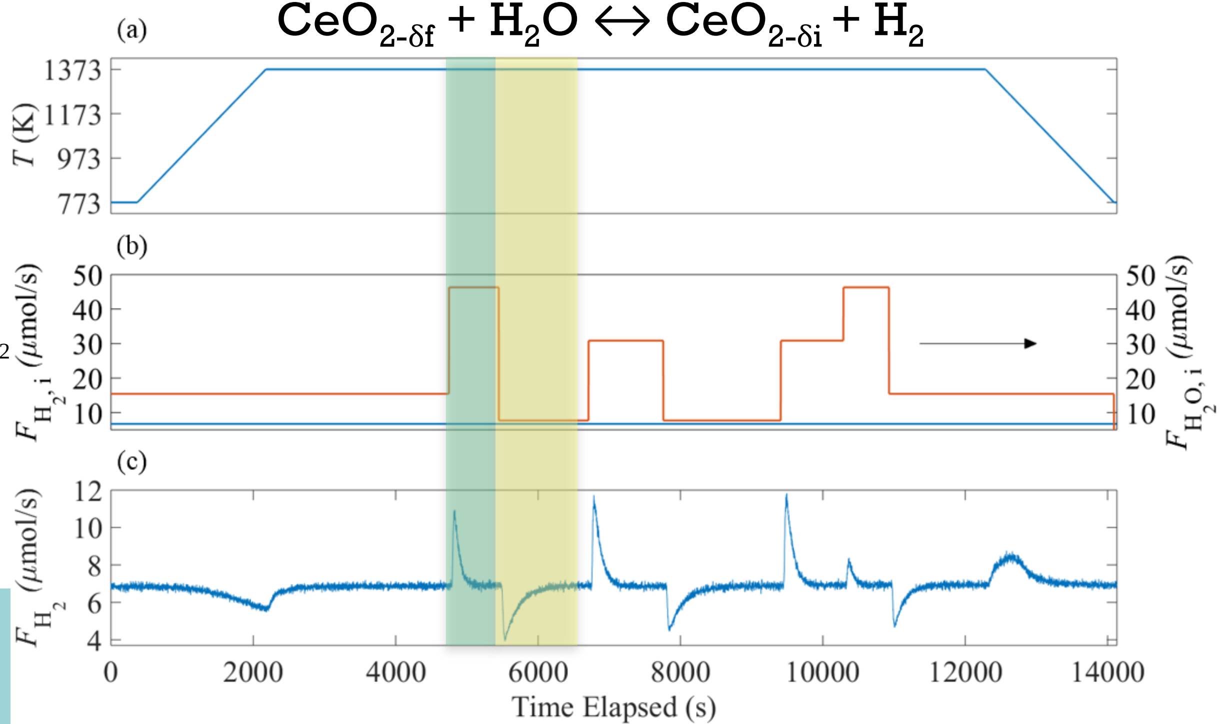


Exemplary Experimental Results

$$CeO_{2-\delta f} + H_2O \leftrightarrow CeO_{2-\delta i} + H_2$$

$$H_2O \rightleftharpoons H_2 + 0.5O_2$$

$$\frac{pO_2}{p^\circ} = \left[K_w(T) \frac{pH_2O}{pH_2} \right]^2$$

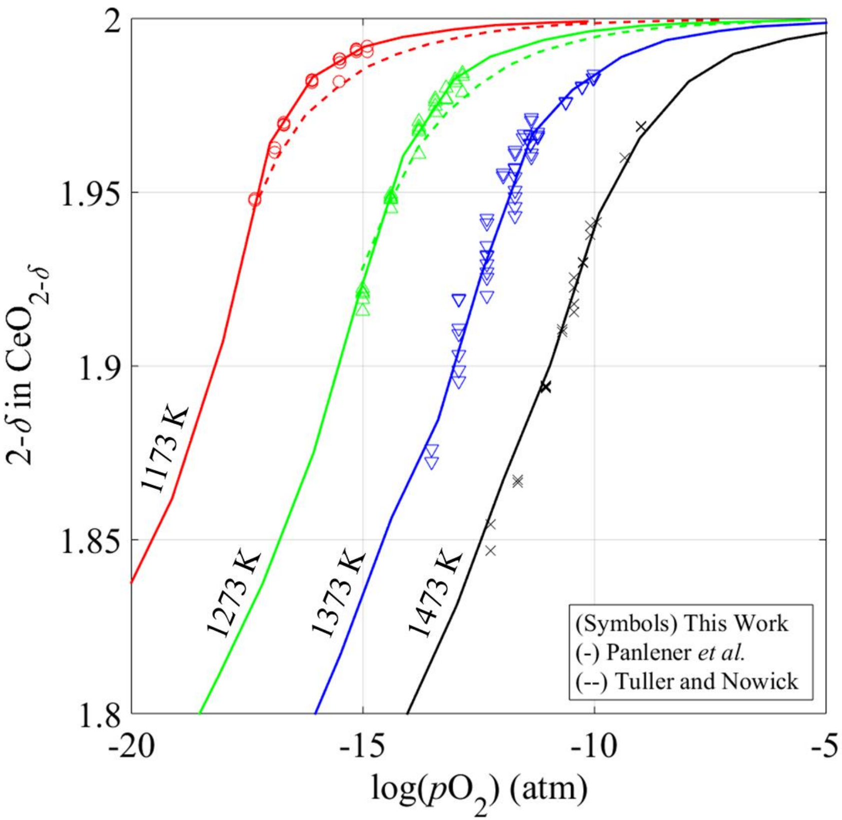


Carrillo, Richard J., Kent J. Warren, and Jonathan R. Scheffe. *Journal of Solar Energy Engineering* 141.2 (2019).

Measured δ Validate the Approach

- Measurements were compared to Panlener *et al.* [1] and Tuller and Nowick [2]

T	1173-1473 K
p **tot**	1 atm
p **O₂**	4.54×10^{-18}-1.02×10^{-9} atm



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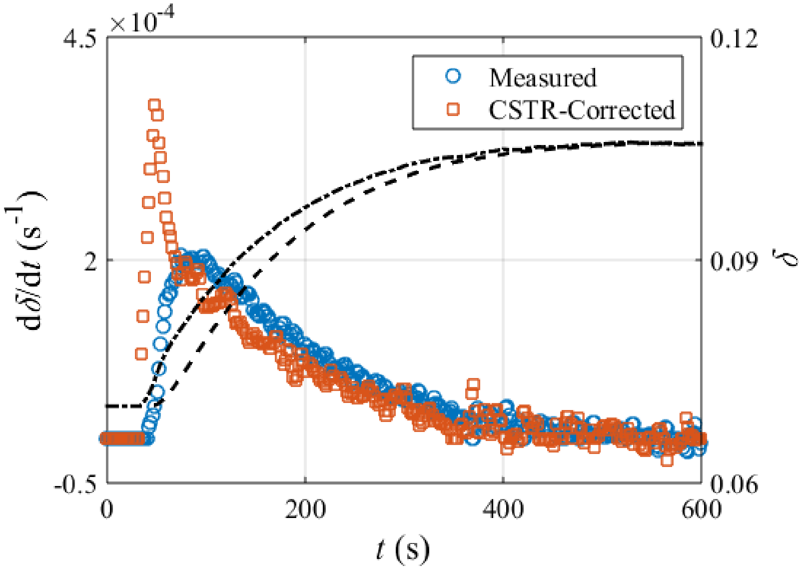
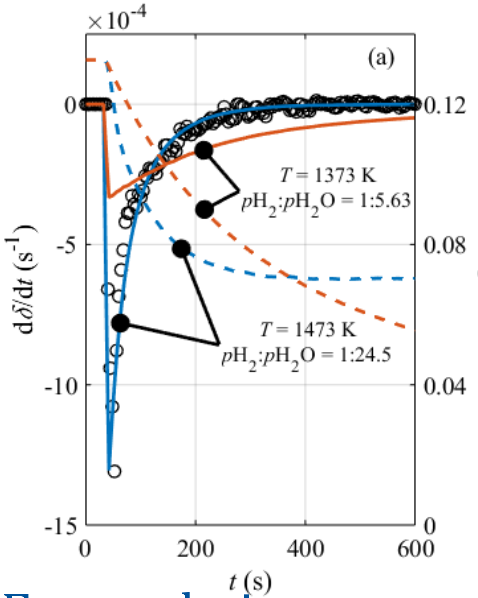
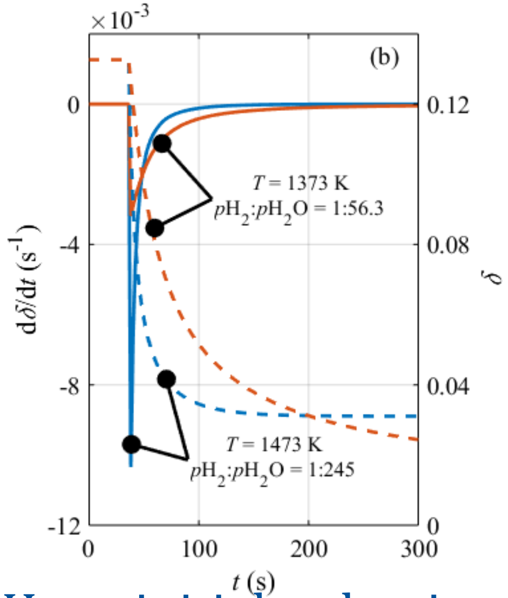
A Good Model Can Serve as a Guide



Correction for gas dispersion



Extrapolation to different conditions



Here, initial reduction extent is greater

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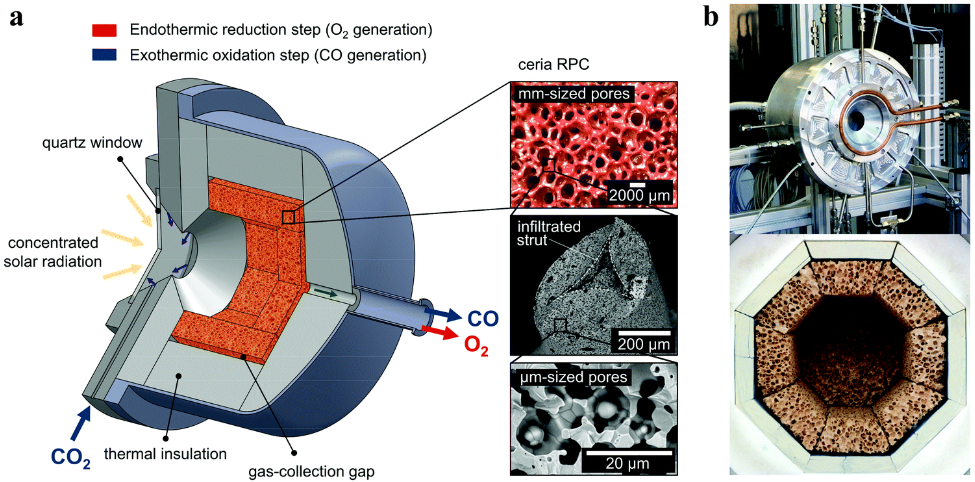
Exemplary Batch Type Reactor

- Marxer et al. has demonstrated highest efficiency to date of 5.3 % using ceria
- 63% of losses due to heating
- Entropy change is dominating factor for temperature swing cycles
- Large pores enhance radiative heat transfer. Usually this is rate limiting during reduction.
- Kinetics usually rate limiting during oxidation with H_2O or CO_2.
- Stability should be demonstrated at this scale because of the extreme thermal gradients.



Marxer, Daniel, et al. "Solar thermochemical splitting of CO 2 into separate streams of CO and O 2 with high selectivity, stability, conversion, and efficiency." *Energy & Environmental Science* 10.5 (2017): 1142-1149.

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